

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
14 June 2001 (14.06.2001)

PCT

(10) International Publication Number  
**WO 01/42415 A1**

(51) International Patent Classification<sup>7</sup>: C11D 3/37, 3/22

(21) International Application Number: PCT/EP00/11819

(22) International Filing Date:  
24 November 2000 (24.11.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
99309884.7 8 December 1999 (08.12.1999) EP

Unilever Research Port Sunlight, Quarry Road East, Bebington, Merseyside CH63 3JW (GB). **HUMPREYS, Karla, Mary**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Merseyside CH63 3JW (GB). **KHOSDEL, Ezat**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Merseyside CH63 3JW (GB). **LIU, Xiang, Yang**; The National University of Singapore, Department of Physics, 10 Kent Ridge Crescent, 119260 Singapore (SG). **RANNARD, Steven**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Merseyside CH63 3JW (GB). **WALLER, Andrew, Mark**; Unilever NV, Weena 455, NL-3013 AL Rotterdam (NL).

(74) Agent: **DEKKER, Enno, E., J.**; Unilever N.V., Patent Department, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(71) Applicant (for AE, AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, FR, GA, GE, GN, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LC, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, NE, NL, NO, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TR, UA, UZ, VN, YU only): **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(71) Applicant (for AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LK, LS, MN, MW, MZ, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London, Greater London EC4P 4BQ (GB).

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (for IN only): **HINDUSTAN LEVER LTD** [IN/IN]; Hindustan Lever House, 165-166 Backbay Reclamation, Mumbai 400 020 (IN).

Published:  
— With international search report.

(72) Inventors: **ASHCROFT, Alexander, Thomas**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Merseyside CH63 3JW (GB). **CARVELL, Melvin**;

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/42415 A1

(54) Title: USE OF POLYMERIC MATERIAL IN THE TREATMENT OF HARD SURFACES

(57) Abstract: Polymeric material is deposited onto hard surfaces to reduce the level of surface heterogeneous nucleation of scale forming calcium salt. Scale is nucleated in the bulk solution, resulting in calcium salts which are easier to remove.

## Use of Polymeric Material in the Treatment of Hard Surfaces

### 5 Introduction

The present invention relates to the use of polymeric material in the treatment of hard surfaces to deal with scale forming calcium salts. Scale is an important soil in  
10 bathrooms and kitchens and one which is not easy to remove.

Household water supplies contain varying levels of calcium and magnesium salts. Residual water left after, e.g.  
~~bathing, showering, dishwashing, rinsing, etc. will~~  
eventually evaporate leading to the deposition of calcium  
15 salts on surfaces as scale.

The scale deposits formed can become unsightly, hard and very difficult to remove. This can happen particularly quickly in hard water areas where the level of calcium in  
20 domestic water is high.

Conventional hard surface cleaners may comprise acid or abrasive in order to assist with the removal of scale. However, enamel and marble surfaces are susceptible to  
25 acid damage and all surfaces may become scratched and unsightly due to the excessive use of abrasive.

Polymeric materials have been used in the water treatment art to prevent precipitation of scale forming salts from  
30 standing water. However, these require a body of water in which the scale forming salts remain suspended. In domestic

hard surfaces, droplets of water containing calcium or magnesium salts will eventually evaporate to dryness and the calcium salts will inevitably be deposited.

5 Attempts have been made in the art to deposit polymeric material onto hard surfaces to allow subsequently deposited soil such as grease to be easily removed.

It has not however been generally believed in the art that  
10 it is possible to provide a release polymer for limescale.

The present inventors have realised that, whereas it may  
~~not be possible to prevent deposition of calcium salts, it~~  
will be possible to control the mechanism of calcium salt  
15 deposition and thereby affect the strength of bond between calcium salts and the hard surface.

Scale can deposit onto household surfaces in two main ways:

- 20 (a) crystallisation in the bulk solution; here, scale can form by homogeneous nucleation or by heterogeneous nucleation onto e.g. dust particles which can act as seeds for nucleation. Bulk heterogeneous nucleation and homogeneous nucleation require high supersaturation  
25 of scale forming salts and can be rapid. Scales formed under these conditions are likely to be amorphous and adhere only weakly to the substrate. Scales which nucleate via bulk heterogeneous nucleation on dust particles can form at lower supersaturations and tend  
30 to form more slowly; they are therefore likely to be

more crystalline but will still adhere only weakly to the household surface.

(b) crystallisation at the hard surface; here,  
5 crystals can form by heterogeneous nucleation in which the household surface acts as the site for nucleation.  
In this case, scale is formed at low supersaturation; the process is comparatively slow and results in crystalline deposits which are compact and intimately  
10 bound to the surface.

The present inventors have realised that a polymeric material can be deposited onto a hard surface to inhibit heterogeneous nucleation at that surface. The majority of  
15 the nucleation will then occur in the bulk solution leading to the deposition of scale forming salts that are easy to remove. The polymer also reduces further aggregation and toughening of new scale on already existing scale deposits.

20 Furthermore it has been found that such polymers provide an anticorrosion benefit when applied to metal surfaces.

Preventing scale from forming or adhering to household  
25 surfaces will retain the smoothness of the surface and prevent it from dulling. This is particularly important for surfaces which are likely to come in extensive contact with water such as can be found in bathrooms, toilets, kitchens and the like. Such surfaces are often made of metal,  
30 vitreous materials or hard plastics.

Summary of the invention

The present invention accordingly provides the use of a polymeric material to reduce heterogeneous nucleation of calcium and magnesium salts at hard surfaces comprising depositing the polymeric material onto the hard surface.

The invention also provides a process for cleaning metal, vitreous and hard plastic surfaces comprising applying to the surface a cleaning composition comprising a detergent surfactant and a polymeric material able to reduce heterogeneous nucleation of calcium and magnesium salts.

15 Detailed description of the inventionPolymeric Material

Many types of polymeric material are suitable for use in the present invention. It is simply required that the polymer is one which, when deposited onto a hard surface at a suitable level, will reduce heterogeneous nucleation of scale forming salts at that surface. Preferably, polymeric material achieves a reduction in the nucleation rate (number of nuclei per unit area per unit time) of scale forming salts at the surface. The following test has been derived to determine whether a polymeric material achieves a reduction in nucleation density (number of nuclei per unit area), which can easily be converted into a nucleation rate if the duration of the experiment is also recorded.

The test comprises applying a solution of polymer of known concentration to a first area sample of a hard surface, providing a second area sample of the hard surface having no polymer thereon and flowing a supersaturated solution of a scale forming salt over each area sample of the hard surface for a known period of time and comparing the number of nuclei formed per unit area per unit time for the area sample treated with the polymeric material with the number of scale nuclei formed per unit area per unit time for the untreated area sample to obtain an estimate of the reduction of the rate of heterogeneous nucleation at the hard surface.

---

#### 15 Brief Description of Drawings

The test for reduction of nucleation density at a hard surface will be described with reference to the accompanying drawings, in which:

20 Figure 1 is a schematic view of apparatus used in the test.  
Figure 2 is a cross-sectional drawing of a mixing device for use in the apparatus of Figure 1.

Figure 3 is a section along line III-III of Figure 2.

Figure 4 shows the motion of fluid on a surface being  
25 tested.

Figure 5 is a picture of a surface which has been tested, the right half having been treated with the polymer.

Detailed Description of Drawings

The apparatus for use in the test for determining whether a polymeric material is suitable for reducing nucleation density at a surface is shown in Figure 1. The apparatus 1 comprises means for delivering two solutions which, when mixed, will produce a supersaturated solution of scale forming salt. The apparatus for delivering the two solutions comprises a pair of syringes 2 and 3. The 10 syringes 2 and 3 contain solutions A and B respectively. In order to ensure that the flow rates of the solutions A and B are the same, a common driving mechanism 4 for both syringes is provided. The mechanism 4 is configured to deliver a constant flow of solutions A and B. The 15 mechanism 4 may comprise a dual drive syringe-type pump which can be obtained from CP Instruments, Model 200. A mixing cell 5, which will be described further below is provided to mix the solutions A and B. The mixed solutions A and B are then directed onto a surface to be tested at 6 20 in a manner which will be described further below. Spent solution is discharged at 7.

All tubing used in the apparatus comprises PTFE tubing for example OD 3.2 mm, ID 1.5 mm obtainable from Omnifit (Trade 25 Mark). The apparatus is jacketed in nitrogen to ensure that carbon dioxide is not reabsorbed.

Figures 2 and 3 show the mixing cell 5 in more detail. Figure 2 is a schematic cross-section, at a larger scale to 30 Figure 1, of the mixing cell 5. The mixing cell 5 comprises a block of PTFE which has a hollow spherical

space 7 formed in its interior. The spherical space 7 is of volume  $1 \text{ mm}^3$ . Projecting through the block and into the space 7 are two capillary tubes, 8 and 9 along which solutions A and B are delivered respectively. The 5 capillary tubes 8 and 9 terminate in nozzles close to the centre of the hollow space 7. The solutions A and B are directed towards one another and mixed in the centre of the hollow space 7. As the block is formed of PTFE, even though a supersaturated solution is formed in the space 7, 10 substantially no adhesion or precipitation of crystalline material onto the surface of the space 7 occurs. The resulting mixed solution leaves the hollow space 7 through a duct 10, whence it is delivered to the experimental surface to be tested at 6. The capillaries 8 and 9 have 15 end openings of 100 micrometres diameter.

Figure 4 shows the apparatus 6 in which the mixture of solutions is directed onto a surface to be tested. The surface 11 to be tested is mounted beneath a nozzle 12, 20 through which the mixed solution from the mixing cell 5 is delivered to the surface 11. The resulting flow pattern is a wall-jet flow pattern, which is well understood by the person skilled in the art. The flow is radially outwards from the centre of the surface 11 to be tested, and is 25 uniform.

The nozzle 12 is a 0.8 mm internal diameter PTFE nozzle placed 3 mm above the surface 11. The mixed solution is delivered at a flow rate of  $4 \text{ cm}^3/\text{min}$ . The wall jet 30 apparatus 6 is jacketed in nitrogen to prevent  $\text{CO}_2$  absorption.



All experiments were carried out in an air-conditioned laboratory. The temperature is measured at the start of each run. Temperatures are typically 23°C.

5

The apparatus allows continual refreshment of the surface with solution of known composition allowing crystal growth to occur under conditions of constant supersaturation.

10

#### Method

~~The apparatus is used to test a surface by the following method.~~

15

A supersaturated solution is created in a manner known to the person skilled in the art by mixing together two stable, undersaturated solutions. The solutions are degassed before use using N<sub>2</sub> to remove dissolved CO<sub>2</sub>.

20

Solution is flowed over the surface to be treated for a fixed time. A suitable time is 45 minutes.

As a result of the flow of solution over the surface 11 to  
25 be tested, scale forming salt is deposited onto the surface. At the end of each experiment, any crystals at the air/water interface are suctioned away using a small piece of tubing attached to a water pump. The surface is then removed from the apparatus 6, rinsed briefly with a  
30 saturated solution of the scale forming salt, dried with nitrogen and inspected under a microscope.

Characterisation of the degree of crystal growth on a surface to be tested can be achieved using a digitised map of the surface produced by micrographics. This map may  
5 then be processed using image analysis software (for example Aequitas, Dynamic Data Links Ltd) which allows automated measurements of crystal size, number and distribution over a choice of area. This allows the nucleation density to be measured.

10

The surfaces to be tested can be prepared and treated in any way as long as the surface remains reasonably flat.  
~~Sample surfaces are preferably polished to a finish of 1/20~~  
micrometres using 0.05 gamma alumina obtainable from  
15 Buehler.

In order to study the effect of polymer deposited onto the surface 11 to be tested, half of the surface is masked and half is treated with a solution or dispersion of the  
20 polymeric material. A 50 microlitre drop of the polymer solution is placed onto the unmasked half of the sample surface and allowed to wet that part of the surface. The drop is left until dry and washed with 10 sprays of deionised water from a trigger spray gun. Drying time may  
25 be from 5 minutes to 20 hours, as appropriate.

Figure 5 shows an example of a map obtainable using the apparatus of the invention, which will be described further below under the section "Examples".

30

10

Preferably, the surface 11 to be tested is in the form of a disc.

Preferably, a set of discs of the same size is used,  
5 consisting of a stainless steel disc, a ceramic disc, an enamel coated disc, a glass disc and a perspex disc.

The nucleation density on the untreated half can then be compared to the nucleation density on the treated half.

10

The experiment may be repeated with different types of calcium salt, for example, calcium carbonate or calcium sulphate or with magnesium salts such as magnesium carbonate or magnesium sulphate.

15

Polymers which are particularly suitable for use in the present invention reduce the nucleation density at the surface by at least 10% on at least one of the test surfaces (glass, steel, ceramic, enamel or perspex) with at  
20 least one of the salts (calcium carbonate, calcium sulphate, magnesium sulphate, magnesium carbonate). More preferably the polymer will reduce the nucleation rate by at least 20%, even more preferably by at least 30% and most preferably by at least 50%.

25

It is further preferred that the polymer should achieve a reduction in nucleation density of at least 10%, more preferably at least 20% with both calcium carbonate and calcium sulphate, on any one of the surfaces, more  
30 preferably on both of steel and glass and most preferably on all of steel, glass, ceramic and enamel.

It has also been found that there is a correlation between the contact angle made by a drop of water on a polymer treated steel surface on the one hand and the ease of  
5 cleaning the steel surface from scale deposits (measured as set out below) and reduction in nucleation density on the other hand. Thus it has been found that polymers which cause the contact angle to be  $< 30^\circ$  or  $> 60^\circ$  cause a significant increase in cleaning score compared with  
10 polymers which cause a contact angle within these limits. Preferred are those polymers which cause the contact angle to be  $< 20^\circ$ , even more preferred are those which cause it to be  $> 60^\circ$  or even  $\geq 65^\circ$ .

---

15 Without being bound by theory it is believed that the contact angle is a manifestation of the surface energy at the interface between water and the polymer-treated surface which in turn determines the degree to which developing scale crystal nuclei are bonded to the surface. It appears  
20 this bonding is strongest for surfaces causing the contact angle to be between  $30^\circ$  and  $60^\circ$

The contact angle made by a drop of water on the treated steel surface can be measured by any of the commonly known  
25 methods. For the purposes of this invention the measurements can be made using a travelling microscope with a simple goniometer head, in which the eyepiece is fitted with crosshairs. A  $20\mu\text{l}$  drop of water is pipetted onto the horizontal treated steel surface. The crosshairs in the  
30 microscope eyepiece are aligned such that the horizontal mark is aligned with the steel surface (i.e., along the

steel/water interface). The centre of the cross is aligned with the three phase contact point (i.e., the water/steel/air interface). The crosshairs are then rotated to align with the edge of the water drop (i.e., along the air/water interface) and the resulting angle is read off on the goniometer scale.

#### Deposition of Polymer Material

10

Polymers for use in the present invention preferably deposit well onto hard surfaces. They may be applied in any way known in the art. Preferably they are applied in the form of a liquid composition containing the polymer in solution or dispersion. More preferably such compositions are aqueous liquids.

Compositions containing the polymers for use in the present invention may be applied in a number of ways, as will be discussed below. For example, they may be applied to a surface and left in contact to evaporate to dryness. In this case, it is simply required that the polymer should be capable of forming a thin and smooth layer, suitably of the order of a few molecular layers of submicron thickness. Other compositions may be applied to the surface with the intention of the surface being subsequently wiped dry. In such cases, it is preferable that the polymer should also have an increased tendency to adsorb to the hard surface.

Examples of compositions containing the polymers are cleaning compositions which have the additional effect of

depositing a polymer for inhibiting nucleation at the surface to be treated. Such compositions will normally contain one or more detergent surfactants in addition to the polymer.

5

It is preferred that the polymer has activity at the solid/liquid interface. It is particularly preferred that the polymer should adhere sufficiently strongly to the surface to be resistant to removal by rinsing. However,  
10 the polymer should not adhere too strongly to the surface, otherwise there may be a tendency for the polymer to build up on the surface which might lead to negative effects, e.g. poor appearance.

---

15 Some surfaces which are particularly prone to scale deposits, such as those made of steel, ceramic, glass and enamel, are known to be negatively charged and it is preferable that the polymer should have cationic groups or groups which become cationic at the pH of use. It is  
20 particularly preferred that the polymer should comprise amine groups, particularly quaternary ammonium or tertiary amine groups.

Deposition of the polymer may also be assisted if it has a  
25 relatively high molecular weight. Preferably, the weight average molecular weight is greater than 5,000, more preferably greater than 10,000, most preferably greater than 50,000.

30 Deposition of the polymer may also be assisted if the polymer or a complex of the polymer with a surfactant is

rigid or semi-rigid. The polymeric material may have an inflexible backbone e.g. due to unsaturation or the presence of rings. Alternatively, it may have a positive charge, either permanently or temporarily at the pH of the composition, restricting conformation of the backbone due to repulsion between charges, or it may have a backbone which is flexible in principle but restricted in molecular conformation derived from polymer architecture, e.g. branching, unsaturation, rings or bulky side groups.

10

If the polymer itself is not net positively charged (for example, if it is negatively charged or neutral),  
~~deposition of the polymer may also be encouraged by the use~~  
of a deposition aid such as a cationically charged polymer  
or surfactant.

15

#### Nucleation Inhibiting Effect

In order to provide a polymer that inhibits nucleation at a surface on which it is deposited, it is preferred that the polymeric material has at least one of the following properties:

1. Hydrophobicity. The polymeric material may have hydrophobic parts. As noted above, in order to enhance deposition of the polymer onto surfaces such as steel, glass, etc., it is preferred that the polymer will also have hydrophilic parts. Accordingly, it is particularly preferred in this case that the polymer is surface active, having hydrophilic and hydrophobic parts on different parts

of the molecule, for example on different sides of the polymer backbone.

Ways of providing hydrophobicity will be discussed below.

5

2. Steric Factors. The inhibition of nucleation may be obtained by steric factors. Preferably, the polymer will comprise large, bulky substituents (for example, incorporating a tertiary carbon atom and/or more than 5  
10 non-hydrogen atoms). Preferably, these are spaced along the polymer backbone at distances which are less than the critical stable microcrystal size. In this way if a microcrystal forms on the surface of the polymer, it will be prevented by steric factors from growing to a size at  
15 which it becomes thermodynamically stable. Preferably, the substituents are unevenly spaced to further inhibit nucleation.

## 20 Solubility

Polymeric materials for use in the present invention are preferably soluble or dispersible in surfactant solution but difficultly soluble or dispersible in water. However,  
25 the polymeric material may also be partially water-soluble and soluble in aqueous surfactant solution of the type used in hard surface cleaning compositions. The solubility of the polymeric material in an aqueous surfactant solution is suitably in the range of 0.01-50% by weight, more  
30 preferably in the range 0.05-10%, most preferably around 0.1-1.0%, particularly 0.4-1.0% by weight. The surfactant



concentration is suitably in the range 0.1-20% by weight, preferably 1.0-10% or 6% by weight.

Polymer Types:

5

The present application may be carried out with many types of polymer of suitable structure to achieve the properties described above. The following non-limiting examples may be given.

10

As a first class, the polymer may be obtained by homo- or copolymerising one or more ethylenically unsaturated monomers, for example ethylenically unsaturated

monocarboxylic acids and their derivatives, for example

15 acrylic acid, methacrylic acid, ethacrylic acid,

acrylonitrile, acrylic acid esters, methacrylic acid

esters, ethacrylic acid esters, alpha-chloro-acrylic acid,

crotonic acid, cinnamic acid, maleic acid, itaconic acid,

citraconic acid, mesaconic acid, glutaconic acid, aconitic

20 acid, fumaric acid, ethylenically unsaturated aromatic

compounds such as styrene and its derivatives, acrylamide,

vinyl acetate, hydroxyethyl acrylate or hydroxypropyl

acrylate.

25 The polymer may additionally comprise a limited amount of non-ionic dye bonding monomers such as N-vinyl substituted heterocycles such as N-vinylimidazole, N-vinylazalactam, N-vinylazalactone, N-vinylpyrrolidone, N-vinylpyridine and vinylpyridine N-oxide.

30

Hydrophilicity can be introduced into the molecule for example by employing acid monomers such as acrylic acid, methacrylic acid etc. However, it is preferred to incorporate ethylenically unsaturated nitrogen containing  
5 monomers which are either cationic or which can become cationic at low pH, for example, monomers such as N,N-dialkylamino-alkyl acrylates and methacrylates, ethylenically unsaturated quaternary ammonium salts such as N,N,N-trimethylamino-ethyl methacrylate methylsulphate or  
10 halide, 2-hydroxy-3-methacryloxypropyl-trimethyl-ammonium methylsulphate or halide, vinylbenzyl-trialkyl-ammonium methylsulphate or halide.

---

The polymer may include acrylamide monomers, such as  
15 acrylamide, N,N-dimethyl-acrylamide or acrylamidoalkylene sulphonic acid.

Polymers suitable for use in the present invention may be produced by any suitable polymerisation method, for example  
20 emulsion or solution polymerisation. Copolymers may for example be produced by graft, block or bulk copolymerisation.

Hydrophobicity may be introduced into polymers for example  
25 by including hydrophobic side chains, such as C<sub>8</sub>-C<sub>22</sub> alkyl, alkenyl or alkylaryl chains. These can be introduced for example as esters of C<sub>8</sub>-C<sub>22</sub> alcohols or the like.

Alternatively, hydrophobicity may be obtained by the use of  
30 an inherently hydrophobic polymer backbone, for example one obtained by polymerising substantially nonionic monomers

such as methyl and ethyl esters of acrylic, methacrylic and ethacrylic acid. In this case, it may be preferred to have hydrophilic substituents to improve substantivity to the surface.

5

Another class of polymers which may be used in the present invention comprises modified natural polymers such as starches and gums. For example, the polymer may comprise guar gum, cellulose, locust bean gum, starch, starch  
10 amylose or similar natural polymers. The natural polymer may be modified by reaction of the hydroxyl groups with other groups, to provide side groups to modify the substantivity of the polymer surface or to provide nucleation inhibiting effects.

---

15

For example, the natural polymer may be modified with nitrogen containing species such as hydroxypropyl-trimethylammonium groups. For example, the polymers may comprise cationic guar gums such as hydroxypropyl-  
20 trimethylammonium guar gum with a degree of substitution in the range 0.11 to 0.22, available commercially under the trade marks JAGUAR C13S, JAGUAR C14S, JAGUAR C17 and JAGUAR C-162.

25 Another class of polymers which may be used in the present invention comprises polyquaternary polymers such as Polyquat 10 which is commercially available under the trademarks Polymer JR30M, JR125 and JR400.

Hydrophobicity may be provided by modifying the natural polymer with, for example, hydrophobic substituents such as C<sub>8</sub>-C<sub>22</sub> alkyl chains, tertiary alkyl groups etc.

### 5 Other Suitable Properties

Preferably, the polymeric material is not highly coloured across the pH range of interest (3-12).

10 Polymers which have been found to significantly reduce the nucleation are given in the table below:

Product name/type (* = Tradename)	Chemical class
Ucare Polymer JR-30M*	Polyquaternium-10-Cationic Hydroxyethyl Cellulose
Jaguar C162*	Hydroxypropyl Guar Hydroxypropyltrimonium Chloride
Lupasol PS*	Modified medium molecular weight PEI
Merquat 280*	80/20 w/w; 64/36 m/m DMDAAC/Acrylic Acid DMDAAC/Acrylic Acid
Crotein C*	Collagen Derivative
Merquat 3330*	25/50/25 w/w; 35/30/35 m/m Acrylic Acid/DMDAAC/Acrylamide
Celquat L200*	Grafted cationic polymer onto a cellulose backbone
Merquat 295*	95/5 w/w; 90/10 m/m DMDAAC/Acrylic Acid DMDAAC/Acrylic Acid
Polymer JR 125*	Polyquaternium-10 - Cationic Hydroxyethyl Cellulose

Polymer JR-400*	Polyquaternium-10 - Cationic Hydroxyethyl Cellulose
Polyacrylic Acid	Polyacrylic Acid
Lup SK*	Modified high molecular weight PEI; Crosslinked and Grafted
Chitosonium betaine	
Jaguar C-13S*	Guar Hydroxypropyltrimonium Chloride
Crodacel*	Quaternised Cellulose derivatives
Croteen O*	Collagen Derivative
Celquat H-100*	Grafted cationic polymer onto a cellulose backbone
Celquat SC240C*	Cationic derivative of hydroxyethyl cellulose
50% QDMCL 50% HPA	
100% QDMCL	
25% DMDMAC 75% AA	
Chitosan acetic acid salt	Chitosan
Chitosan 4-hydroxy-L-proline	Chitosan
Chitosan lactobionic acid	Chitosan
Chitosan 2-hydroxycaprylate	Chitosan
PVA 130K*	Polyvinyl Alcohol
PVA 205K*	Polyvinyl Alcohol

Other polymers which are chemically equivalent to the polymers mentioned above may be used instead. Such polymers are known the person skilled in the art.

Hard Surface Treatment Compositions

The polymeric material can be used according to the present  
5 invention in any suitable formulation.

The formulation must be suitable for depositing the  
polymeric material onto a hard surface. The polymeric  
material may be present in the formulation in any suitable  
10 form, for example in the form of a solution or dispersion.

Suitable formulations include solutions, dispersions or  
emulsions of the polymeric material in a carrier, for  
example a substantially non-aqueous material such as  
15 ethanol, but preferably water. The compositions may be  
used only to deposit polymeric material, or they may have  
additional functions such as cleaning.

The composition may be applied by any suitable means. For  
20 example, it can be poured or sprayed onto the surface from  
a container or from an aerosol can or from a spray gun  
applicator.

Compositions for use in the present invention may include  
25 any normal ingredients for hard surface cleaning  
compositions.

Preferably, a hard surface cleaning composition comprises  
at least one detergent surfactant and optional other hard  
30 surface cleaning components.

### Surfactants:

The composition according to the invention will comprise detergent actives (surfactants) which are generally chosen from both anionic and nonionic detergent actives.

Suitable anionic surfactants are water-soluble salts of organic sulphuric acid esters and sulphonic acids which have in the molecular structure an alkyl group containing from 8 to 22 carbon atoms.

Examples of such anionic surfactants are water soluble salts of:

- long chain (i.e. 8-22 C-atom) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols produced by reducing the glycerides of tallow or coconut oil;
- alkyl benzene sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
- 20 - secondary alkanesulphonates.

Also suitable are salts of:

- alkyl glyceryl ether sulphates, especially those ethers of the fatty alcohols derived from tallow and coconut oil;
- 25 - fatty acid monoglyceride sulphates;
- sulphates of the reaction product of one mole of a fatty alcohol and from 1 to 6 moles of ethylene oxide;
- salts of alkylphenol ethyleneoxy-ether sulphates with from 1 to 8 ethyleneoxy units per molecule and in which
- 30 the alkyl groups contain from 4 to 14 carbon atoms;

- the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali; and mixtures thereof.

- 5 The preferred water-soluble synthetic anionic surfactants are the alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of alkylbenzenesulphonates and mixtures with olefinsulphonates and alkyl sulphates, and the fatty acid mono-glyceride sulphates.
- 10 The most preferred anionic surfactants are alkylaromatic sulphonates such as alkylbenzenesulphonates containing from 6 to 20 carbon atoms in the alkyl group in a straight or branched chain, particular examples of which are sodium salts
- 
- of alkylbenzenesulphonates or of alkyl-toluene-, -xylene- or
- 15 -phenolsulphonates, alkyl-naphthalene-sulphonates, ammonium diaminonaphthalene-sulphonate, and sodium dinonylnaphthalene-sulphonate.

If synthetic anionic surfactant is to be employed the amount

20 present in the compositions of the invention, it will generally be at least 0.5%, preferably at least 1.0%, more preferably at least 2.0%, but not more than 20%, preferably at most 10%, more preferably at most 8%

- 25 Suitable nonionic surfactants can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene
- 30 radical which is attached to any particular hydrophobic group can be readily adjusted to yield a water-soluble compound



having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of nonionic surfactants with the right HLB, taking into account the presence of the organic solvent and possible hydrocarbon co-solvent in the composition.

Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol; condensates of the reaction product of ethylenediamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 5,000 to 11,000.

Other examples are: Alkylglycosides which are condensation products of long chain aliphatic alcohols and saccharides; tertiary amine oxides of structure  $RRRN_0$ , where one R is an alkyl group of 8 to 18 carbon atoms and the other Rs are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyldodecylamine oxide; tertiary phosphine oxides of structure  $RRRP_0$ , where one R is an alkyl group of 8 to 18 carbon atoms and the other Rs are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide; and dialkyl sulphoxides of structure  $RRS_0$  where one R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance

methylnonadecyl sulphoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid alkylolamides and alkyl mercaptans. Ethoxylated aliphatic alcohols are particularly preferred.

5

The amount of nonionic surfactant to be employed in the cleaning composition of the invention will preferably be at least 0.2%, more preferably at least 0.5%, most preferably at least 1%. The maximum amount is suitably 15%, preferably 10% and most preferably 7%.

The compositions may contain amounts of both anionic and nonionic surfactants which are chosen, bearing in mind the level of electrolyte present, so as to provide a structured liquid detergent composition, i.e. one which is 'self-thickened'. Thus, in spite of the presence of organic solvent, thickened liquid cleaning compositions can be made without the need to employ any additional thickening agent and which nevertheless have a long shelf life over a wide temperature range.

The weight ratio of anionic surfactant to nonionic surfactant may vary, taking the above considerations in mind, and will depend on their nature, but is preferably in the range of from 1:9 to 9:1, more preferably from 1:4 to 4:1, and ideally above 1:1.

According to an embodiment, illustrating this aspect of the invention, the cleaning compositions will comprise from 0 to 10% by weight of a water-soluble, synthetic anionic sulphate or sulphonate surfactant salt containing a C<sub>8</sub>-C<sub>22</sub> alkyl

group, and from 0.5 to 7% by weight of an ethoxylated alcohol nonionic surfactant having a C<sub>8</sub>-C<sub>22</sub> alkyl group and 2 to 15 ethyleneoxy groups.

5 It is also possible optionally to include amphoteric, cationic or zwitterionic surfactants in the compositions according to the invention.

Suitable amphoteric surfactants that optionally can be  
10 employed are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane sulphonate and  
15 sodium N-2-hydroxydodecyl-N-methyl taurate.

Suitable cationic surfactants are quaternary ammonium salts having one or two aliphatic groups of from 8 to 18 carbon atoms and two or three small aliphatic (e.g. methyl) groups,  
20 for instance cetyltrimethyl ammonium bromide.

Suitable zwitterionic surfactants that optionally can be employed are derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic  
25 group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance 3-(N,N-dimethyl-N-hexadecylammonium) propane-1-sulphonate betaine, 3-(dodecyl methyl sulphonium) propane-1-sulphonate betaine and 3-(cetylmethyl phosphonium) ethane  
30 sulphonate betaine.

Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks "Surface Active Agents", Volume I by Schwartz and Perry and "Surface Active Agents and Detergents", Volume 5 II by Schwartz, Perry and Berch.

If surfactants are to be present in the compositions of the present invention, the total amount of surfactant compound to be employed will generally be from 0.5 to 20%. Preferably the amount is at least 1%, more preferably at least 3%. The maximum amount is usually 15% or less, preferably not more than 10%. Preferably the kind of surfactant and its amount is chosen such that it does not form a complex with the polymer which cannot be maintained dissolved or dispersed in the composition.

The compositions according to the present invention may contain other ingredients which aid in their cleaning performance. For example, the compositions may contain insoluble abrasives such as calcites, silica and other abrasive materials known in the art, or they may contain detergency builders such as nitrilotriacetates, polycarboxylates, citrates, dicarboxylic acids, water-soluble phosphates (especially ortho-, pyro- or polyphosphates or mixtures thereof), zeolites and mixtures thereof in an amount of up to 25%. Some of these builders can additionally function as abrasives if present in an amount in excess of their solubility in water. If present, the builder preferably will form at least 0.1% of the composition.

Metal ion sequestrants such as ethylenediaminetetraacetates, amino-polyphosphonates (DEQUEST<sup>TM</sup>) and phosphates and a wide variety of poly-functional organic acids and salts, can also optionally be employed provided they are compatible with  
5 polymer and optional abrasive material.

A further optional ingredient for compositions according to the invention is a suds regulating material, which can be employed in compositions which have a tendency to produce  
10 excessive suds in use. One example of a suds regulating material is soap. Soaps are salts of fatty acids and include alkali metal and ammonium salts of fatty acids containing  
~~from about 8 to about 24 carbon atoms,~~ and preferably from about 10 to about 20 carbon atoms. Particularly useful are  
15 the sodium and potassium and mono-, di- and tri-ethanolamine salts of the mixtures of fatty acids derived from coconut oil and groundnut oil. When employed, the amount of soap can form at least 0.005%, preferably 0.1% to 2% by weight of the composition. A further example of a suds regulating material  
20 is silicone oil.

A further optional ingredient which may be used in compositions according to the invention is an acidic material which helps in removing scale deposits. Examples thereof are  
25 well known in the art and include phosphoric acid and many di- and polycarboxylic acids.

Compositions according to the invention can also contain, in addition to the ingredients already mentioned, various other  
30 optional ingredients such as colourants, whiteners, optical brighteners, soil suspending agents, deterative enzymes,

compatible bleaching agents such as active chlorine compounds or hydrogen peroxide, gel-control agents, freeze-thaw stabilisers, bactericides, preservatives (for example 1,2-benzisothiazolin-3-one), perfumes and hydrotropes.

5

The hard surface treatment composition can have any suitable pH. However, it is preferred that compositions are either mildly alkaline (particularly if they are formulated as surface cleaning compositions, in order to enhance the  
10 effect of surfactants), neutral or slightly acidic (particularly if they include cationic species or amine groups which become protonated and cationic in an acid environment, in order to assist deposition). However, it is preferred that the compositions should not be too  
15 acidic, in order to avoid damage to acid sensitive surfaces. In particular, it is important to minimise or avoid the presence of sequestering organic acids which are prone to attack surfaces such as enamel. Preferably the pH is in the region 3-12, with the ranges 3.5-6.0 and 10-12  
20 being particularly preferred. In any event, the pH is suitably above 3.0 and more preferably above 3.5.

Use of polymeric material according to the present invention can, in addition to scale inhibiting effects,  
25 give a longer lasting shine, better surface appearance, a smooth feel to treated surfaces.

Compositions according to the present invention are useful for treating household surfaces in for example kitchens and  
30 bathrooms, including walls, floors, toilets, dishwashers, and work surfaces. They are particularly suitable for

treating surfaces which are prone to remain in prolonged contact with water such as: shower walls and floors, bath tubs and rims, taps, shower heads, wash basins, sinks and the like.

5

The present invention will be described further by way of reference to the following non-limiting examples.

#### Examples

10

All percentages mentioned herein are by weight based on the total composition unless specifically mentioned otherwise.

---

Surface treatment compositions were prepared according to the following formulations (\* indicate the nucleation inhibiting polymers):

#### Example 1 - Cleaning Mousse

20 Dobanol 23 6.5EO <sup>TM</sup>	2.5%
2-Butoxy ethoxy ethanol	2.0%
Tri-sodium citrate	4.0%
Sodium hydroxide	0.015%
Alkaline sodium silicate	0.2%
25 Perfume	0.4%
Ammonium hydroxide	0.057%
Propellant	6%
*Polyethyleneimine (Lupasol PS <sup>TM</sup> ex BASF)	0.5%
Water to	100%

30

31

Example 2 - Bathroom cleaning formulation

Alcohol Ethoxylate 8EO	6.00
Dicarboxylic Acids	4.00
5 2-butoxy ethoxy ethanol	2.00
Phosphoric Acid	0.50
Coconut Fatty Acid	0.25
Magnesium Sulphate 7H <sub>2</sub> O	1.00
Sodium Hydroxide	0.34
10 1,2 Benzisothiazolin -3-one	0.016
Perfume	0.50
*Polymer JR-30M	0.50
Water	to 100

---

15

Example 3 - Bathroom cleaning formulation

Alcohol Ethoxylate 8EO	6.00
Dicarboxylic Acids	4.00
20 2-butoxy ethoxy ethanol	2.00
Magnesium Sulphate 7H <sub>2</sub> O	1.00
*Polymer Jag C162	0.50
Water	to 100

25



Tests for Ease of Removal of Scale from Treated Surfaces

Steel tiles formed of certain surfaces are obtained from Mersey Metals. The tiles were 0.9 mm thickness, 100 x 100 mm square in size, finished to 304 specification with a mirror finish and plastic backed on one side. The tiles are thoroughly cleaned and rinsed using demineralised water. The tiles are then left to dry.

10 A 0.5% by weight aqueous solution of polymer is applied in an even layer to each tile using a K-bar applicator, K-bar number 0010. 0.5 ml of solution is pipetted across the top edge of the tile next to the K-bar. The driving speed of the K-bar is set to 16.5 cm/s.

15

The tiles are left to dry for up to 24 hours.

Dried tiles are then mounted at 10° to the horizontal. Each tile is then rinsed with 200 ml of demineralised water  
20 pumped across the tile by a peristaltic pump at a rate of 812 ml/min. The tile is then laid horizontally to dry.

Plastic templates in the form of square sheets of acetate film having a square hole in the centre are adhered to each  
25 tile. 0.5 ml of Prenton water (27°FH) is added to each tile within the square defined by the plastic template. The drop is left to dry. The step is repeated for 6 x 0.5 ml additions of Prenton water, each of which is left to dry. The treated tiles are then subjected to a cleaning  
30 test using a WIRA (Wool Institute Research Association) machine. This apparatus measures the number of cycles

required to clean a defined area. The area to be cleaned corresponds to the exposed area defined by the plastic template. The tiles are cleaned using a damp J-cloth<sup>TM</sup> on a WIRA machine which is operated for 4 cycles (16 x 4 = 64 strokes under the maximum load). Once cleaned, the tiles are left to dry and assessed for scale, and tarnish. Scale and tarnish are assessed subjectively and rated on a scale of 1 to 4, 1 corresponding to no or very little removal and 4 corresponding to a completely clean surface.

10

### Results

~~The method of Example 3 is conducted with the polymeric~~  
 materials listed in the table below. The tarnish results  
 15 were assessed and the scores are set out below.

<u>Treatment</u>	<u>Average score</u> (uncertainty at 95% confidence limit in brackets)
Jif (trade mark) cleaned	1.93(7)
Surfactant cleaned only	1.7(2)
Merquat 3330 (trade mark)	2.9(5)
Merquat 295 (trade mark)	3.0(7)
Celquat L200 (trade mark)	2.9(3)
Lupasol PS (trade mark)	3.7(3)
Lupasol SK (trade mark)	3.7(2)
JR-30-M (trade mark)	3.6(2)
Jaguar C162 (trade mark)	3.4(4)
Crotein C (trade mark)	3.6(4)

Measurement of nucleation density

The apparatus described above for measuring nucleation density can be used to test the effect of polymer on nucleation density at a surface, as follows.

A 10 mm diameter stainless steel sample (steel type 304) polished to a 0.05 micrometre finish was masked on one half. The other half was treated with a 0.5%wt aqueous solution of polymer.

Solution A comprises calcium chloride (obtained from Aldrich 99.99% plus pure) in 0.1 MNaCl (obtained from Fisons, 99.9% plus pure) and solution B comprise NaHCO<sub>3</sub> (obtained from BDH, 99.5% plus pure) in 0.1 MNaCl. The concentrations of calcium chloride and sodium bicarbonate are altered to achieve supersaturation of calcium carbonate in a manner known to the person skilled in the art.

20

The pH is regulated to 8.5 using NaOH (obtainable from Fisons, 86% plus pure) or HCl (obtainable from Aldrich, 0.5098 N, ACS grade).

25 The experiment was repeated with a number of different types of polymer. The results are shown in the following table:

30

<u>Polymer</u> (all indicated by trademark)	<u>Number of</u> <u>crystals</u> <u>per m<sup>2</sup></u> <u>treated</u> <u>half</u>	<u>Number of</u> <u>crystals</u> <u>per m<sup>2</sup></u> <u>untreated</u> <u>half</u>	<u>Ratio of</u> <u>nuclea-</u> <u>tion</u> <u>density</u>	<u>% reduction</u> <u>in</u> <u>nucleation</u> <u>density</u>
Lupasol PS	9.432e7	3.035e8	1:3.2	69%
Celquat L200	5.280e7	2.139e8	1:4.1	75%
JR-30M	1.630e8	2.934e7	1:5.6	82%
Lupasol SK	1.318e9	3.953e9	1:3.0	67%
Ucare LK	5.128e8	1.439e9	1:2.8	64%
Alcogum L520	3.876e8	6.431e8	1:1.7	40%
Narlex ST15	1.852e9	8.718e8	1:0.5	-112%

Figure 5 shows a map obtainable using the apparatus and software described above. The map is obtained for a sample treated with Lupasol (trade mark).

The map of the substrate shows a clear difference between the treated (right hand) and untreated (left hand) halves. Image analysis shows that the total density of crystals on the untreated half is 9.432e7 whereas the treated half has 3.035e8. The mean crystal size for the untreated half was 15 mm<sup>2</sup> and for the treated half it was 17 mm<sup>2</sup>. It can be seen that the treatment of the surface with Lupasol solution (trade mark) has resulted in a reduction in the

36

number of crystals grown by a factor of 3 compared to the number on the untreated portion. The crystals grown on the treated half are very similar in size to those on the untreated half. This means that far less material has 5 grown on the treated half.

10

---

### Claims

1. The use of a polymeric material to reduce heterogeneous nucleation of calcium and magnesium salts at a hard surface comprising depositing the polymeric material onto the hard surface.
2. The use according to claim 1, comprising using a polymeric material which achieves a reduction of nucleation density at the hard surface of at least 10% with at least one salt selected from the group consisting of calcium carbonate, calcium sulphate, magnesium sulphate, magnesium carbonate and mixtures thereof, in the method described herein.
3. The use according to claim 2, wherein a polymeric material is used which achieves a reduction in nucleation density of at least 10%, more preferably at least 20% with both calcium carbonate and calcium sulphate on any surface selected from the group consisting of steel, glass, ceramic and enamel.
4. The use according to any preceding claim, wherein a polymeric material having activity at a solid/liquid interface is used.
5. The use according to claim 4, wherein the polymeric material has cationic groups or groups which become cationic at the pH of use.

6. The use according to any preceding claim, wherein the polymeric material has hydrophobic parts.

7. The use according to any preceding claim, wherein the polymeric material is deposited from a container, aerosol can or spray gun applicator.

8. The use according to any preceding claim, wherein the polymeric material is deposited from a hard surface cleaning composition comprising at least one surfactant and other optional hard surface cleaning components.

---

9. The use according to any preceding claim, for treating household surfaces selected from the group consisting of kitchen surfaces, bathroom surfaces, floors, baths, toilets, wash hand basins, showers, dishwashers, taps, sinks and work surfaces.

10. The use according to any preceding claim wherein the surface is made from metal, vitreous material or hard plastic.

11. The use according to any preceding claim wherein the polymer is chosen from those which cause the contact angle of a drop of water on a steel surface treated with the polymer to be less than  $30^\circ$  or more than  $60^\circ$ .

12. The use according to any preceding claim wherein the polymer is chosen from: JR30m, JR125, JR400, Jaguar C13s, Jaguar C162, Crotein C, Lupasol PS, Lupasol SK, Celquat L200, Merquat 3330, Merquat 295 or mixtures thereof.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/11819

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/37 C11D3/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 60086 A (PROCTER & GAMBLE) 25 November 1999 (1999-11-25)	1,4-10
A	page 1, paragraph 3 -page 3, paragraph 5 page 14, paragraphs 4,5 page 16, paragraph 1 -page 18, paragraph 2 page 20, paragraphs 1,2 page 36, paragraph 4 -page 39, paragraph 1 ---	2,3,12
X	EP 0 875 555 A (PROCTER & GAMBLE) 4 November 1998 (1998-11-04)	1,4, 7-10,12
A	page 4, line 30 -page 5, line 1 examples claims 1,6 ---	2,3
A	EP 0 635 567 A (KODAK) 25 January 1995 (1995-01-25) the whole document ---	1,8,9
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

21 March 2001

Date of mailing of the international search report

30/03/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Bertran Nadal, J

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/11819

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 679 592 A (SCHOMBURG NOEL L) 25 July 1972 (1972-07-25) the whole document ---	1-4, 7-9
A	WO 94 26858 A (UNILEVER) 24 November 1994 (1994-11-24) page 5, line 10 -page 7, line 27 examples 1-4 ---	1, 5-10, 12
A	EP 0 342 997 A (UNILEVER) 23 November 1989 (1989-11-23) page 3, line 40 -page 4, line 6 examples 1-4 ---	1, 5-12
A	EP 0 843 003 A (KAO CORP) 20 May 1998 (1998-05-20) page 9, line 2-57 -----	1, 5-10, 12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. .onal Application No

PCT/EP 00/11819

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9960086 A	25-11-1999	EP 0957156 A	17-11-1999
EP 0875555 A	04-11-1998	WO 9849260 A	05-11-1998
EP 0635567 A	25-01-1995	NONE	
US 3679592 A	25-07-1972	NONE	
WO 9426858 A	24-11-1994	AU 698794 B	05-11-1998
		AU 6648394 A	12-12-1994
		BR 9406406 A	19-12-1995
		CZ 9503024 A	13-03-1996
		DE 69401815 D	03-04-1997
		DE 69401815 T	12-06-1997
		EP 0699226 A	06-03-1996
		ES 2098939 T	01-05-1997
		HU 73043 A, B	28-06-1996
		JP 2750001 B	13-05-1998
		JP 8510276 T	29-10-1996
		KR 221768 B	15-09-1999
		PL 311696 A	04-03-1996
		SK 140195 A	06-03-1996
		ZA 9403260 A	13-11-1995
EP 0342997 A	23-11-1989	AU 619545 B	30-01-1992
		AU 3480789 A	23-11-1989
		BR 8902331 A	09-01-1990
		DE 68917371 D	15-09-1994
		DE 68917371 T	01-12-1994
		ES 2058522 T	01-11-1994
		JP 2018499 A	22-01-1990
		JP 2857168 B	10-02-1999
		KR 9600201 B	03-01-1996
		TR 25242 A	01-12-1992
		ZA 8903779 A	30-01-1991
EP 0843003 A	20-05-1998	US 6117830 A	12-09-2000
		CN 1196752 A	21-10-1998
		WO 9742296 A	13-11-1997
		JP 2826099 B	18-11-1998
		JP 10273697 A	13-10-1998